

# Long-term TNT and DNT contamination: 1-D modeling of natural attenuation in the vadose zone: case study, Portugal

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**Abstract** The vadose zone of a trinitrotoluene (TNT) and dinitrotoluene (DNT) contaminated site was investigated to assess the mobility of those explosives under natural conditions. Located in the left margin of the River Tejo Basin, Portugal, the site is located on unconsolidated sediments. Wastewaters associated with the 50-year explosives production were disposed in excavated ponds, from where water would infiltrate and pollute the unsaturated and saturated parts of the local aquifers. Two boreholes were drilled to 9 m depth in such a former waste pond to investigate the contaminant's fate in the vadose zone. Sediment samples were taken every 1–2 m for analysis of the polynitroaromatics (p-NACs) and organic volatile compounds, pH, organic carbon content, cation exchange capacity and grain size analysis. The main contaminant was TNT representing >70 % of the total p-NACs concentration that peaked approximately 7 mg/kg in one borehole, even if the median in both boreholes was of ~1 mg/kg. DNT was 4–30 % of the total p-NACs and nitrotoluene (NT), up to

5 %. No other (volatile) organic compound was detected. The predominance of TNT as the main contaminant implies that any natural mass reduction has been inefficient to clean the site. Several 1-D model simulations of p-NACs cleaning of the vadose zone under natural conditions indicated that the most probable scenario of combined advection and partitioning will only remove TNT after 10's of years, whereas DNT and NT will hardly be removed. Such low concentrations and long times for the p-NACs removal, suggest that by now those compounds have been washed-out to a level below standard limits.

**Keywords** Soil contamination · Explosives · Vadose zone · 1-D modeling · Natural attenuation

## Introduction

### Case study: explosive production

Trinitrotoluene (TNT) was first synthesized by the end of the nineteenth century and began to be massively produced in 1916, in the USA (EPA 2012b). TNT is obtained by the sequential nitration of toluene by a mixture of nitric and sulphuric acids (ATSDR 1995). Dinitrotoluene (DNT) is mainly an explosive intermediate, produced also by nitration and/or being the result of TNT transformation (ATSDR 1998). TNT and DNT can also be associated to ammunition residues in range training areas (Brannon and Pennington 2002).

During about 50 years (1949–1998), the manufacturing of the explosives TNT (and DNT) south of the Lisbon metropolitan area (Portugal, Fig. 1a), contaminated the soil and the groundwater within and downstream of the production site. Such contamination is believed to have occurred due to the large release of wastewater saturated

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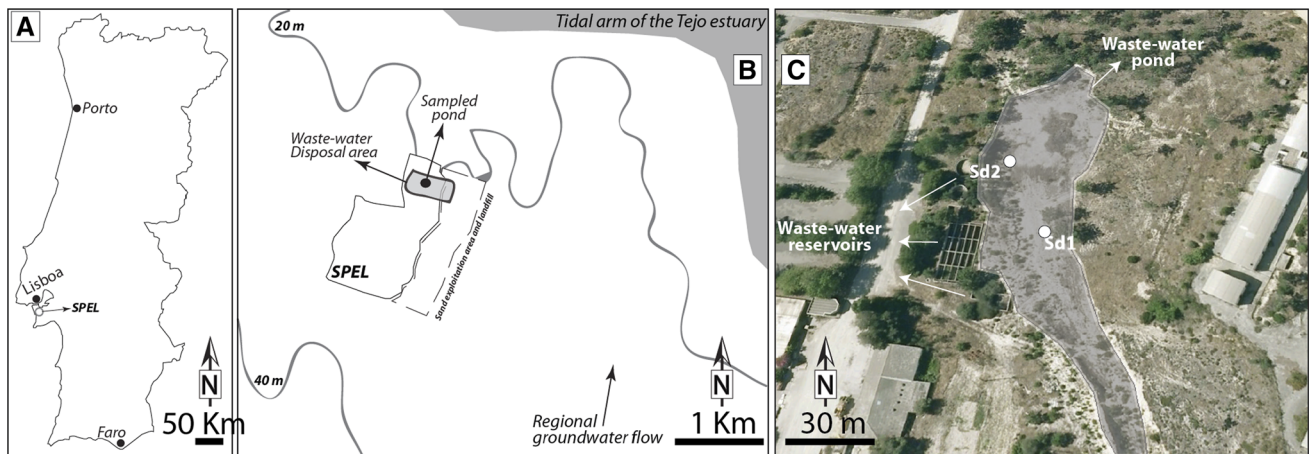
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**Fig. 1** **a** Map of Continental Portugal indicating the main cities and the location of SPEL (explosive production site); **b** SPEL area (in white and delimited by a black line) and the location of the sampled ex-pond within the ex-wastewater disposal area (adapted from Amaral et al. 2009)—indicated is also the regional groundwater flow in the direction of the Tejo River; **c** location of the two boreholes (Sd1 and

Sd2, white dots) drilled inside the dried explosives wastewater pond (grayish polygon). Also marked are the reservoir-tanks (indicated by the white arrows) where the contaminated waters were collected and released to the pond, whenever overflowing (back image from Google Earth, 2014)

with TNT and DNT (generally referred to as pink water), as well as other nitrated organics that would be discharged, without treatment, to disposal pits and runoff ditches (Fig. 1b, c). It is unknown whether those pits would be year-round filled with wastewater and/or if there was any sediment remobilization within the pits. The major part of the wastewaters would have infiltrated into the ground. The other part would have evaporated leading to the formation of a solid residue of explosives on the soil surface. It is suggested that the residue could have become a reservoir for leaching of explosives through the soil profile into groundwater, with each rainfall event. No wastewater treatment has been reported.

The historical documentation on the production of explosives at the site is scarce. Nevertheless, it was estimated that 300–900 tons of DNT and ~400 tons of TNT were produced annually, accompanied by 0.2 tons and 10 tons of waste, respectively (INETI and ITA 1996). The available reports indicate that no other typical energetic compounds such as royal demolition explosives (RDX, 1,3,5-Trinitroperhydro-1,3,5-triazine) and high melting explosives (HMX, Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) were produced at the site (Table 1).

### Hydrogeological setting

Located in the River Tejo Left Margin multi-layered aquifer system (Almeida et al. 2000), the studied area encompasses heterogeneous fluvial sediments, which being quite permeable led to a poorly developed surface drainage. The climate is relatively dry, with an average annual air temperature of about 16 °C. The surrounding vegetation

consists of dry grasses, pine trees and eucalyptus. No perennial streams flow within the studied area.

A previous study (Amaral et al. 2009) showed that groundwater contamination by the aforementioned explosives was detected away from the site, in both the upper unconfined sandy aquifer and in the lower semi-confined calc-arenitic aquifer. The geological formations are described in detail in Ribeiro (2009). In the most contaminated well, TNT reached ~33 mg/L and the total of poly-nitroaromatics (p-NACs) reached ~44 mg/L. The combined use of the N- and C-isotopes assessed that within the 3 most contaminated wells, no biotransformation has taken place as virtually no isotopic fractionation was observed (Amaral et al. 2009). Thus, the most probable processes affecting the fate of the p-NACs in groundwater are the combination of adsorption (onto clay minerals, hydroxides and oxides, and onto organic materials within the aquifer matrix), groundwater pumping (even if many wells started to operate much after contamination started), and transport by diffusion, advection and/or dispersion.

Groundwater used for public supply was shown to be contaminated by p-NACs, (Amaral et al. 2009) after which, the Portuguese authorities stated the need for this site to be characterized for remediation (APA and ARH-Tejo 2012). It has been reported that military sites represent about 3 % of local contamination source (Liedekerke et al. 2014), amongst the many cases of soils contaminated by explosives as the result of WWII activities and/or remnants (see for example Beller et al. 2004; Duque et al. 1993; Preuss and Haas 1988). However, there is a lack of field data considering the number of reports on other types or organic contamination. The case study being presented in this

**Table 1** Chemical properties of the p-NACs detected in the study area. Values compiled from EPA (2012a, b, c, d)

Properties	2,4,6-TNT Cas no. 118-96-7	2,4-DNT Cas no. 121-14-2	2,6-DNT Cas no. 606-20-2	2-NT (NT, o-) Cas no. 88-72-2	4-NT (NT, p-) Cas no. 99-99-0
Chemical formula	C <sub>7</sub> H <sub>5</sub> N <sub>3</sub> O <sub>6</sub>	C <sub>7</sub> H <sub>5</sub> N <sub>3</sub> O <sub>6</sub>	C <sub>7</sub> H <sub>5</sub> N <sub>3</sub> O <sub>6</sub>	C <sub>7</sub> H <sub>7</sub> NO <sub>2</sub>	C <sub>7</sub> H <sub>7</sub> NO <sub>2</sub>
Molecular weight (g/mol)	227	182	182	137	137
Density (g/cm <sup>3</sup> )	1.66	1.32	1.28	1.16	1.39
Aqueous solubility (mg/L)	130	270	180	440	350
Octanol–water partition coefficient <i>K</i> <sub>ow</sub> (Log) (–)	1.60	1.98	2.10	2.30	2.37
Carbon–water partition coefficient <i>K</i> <sub>oc</sub> (Log) (–)	1.10	1.65	1.96	2.62	2.49
Vapor pressure (mm Hg)	1.99 × 10 <sup>-4</sup> (25 °C)	1.5 × 10 <sup>-2</sup> (22 °C)	5.67 × 10 <sup>-4</sup> (22 °C)	1.88 × 10 <sup>-1</sup> (25 °C)	9.75 × 10 <sup>-2</sup> (20 °C)
Henry's constant (atm m <sup>3</sup> /mol)	4.57 × 10 <sup>-7</sup>	8.79 × 10 <sup>-8</sup>	9.26 × 10 <sup>-8</sup>	1.25 × 10 <sup>-5</sup>	5.63 × 10 <sup>-6</sup>
Residential soil (max. allowed) (mg/kg)	19	1.6	0.3	2.9	30
Industrial soil (max. allowed) (mg/kg)	79	5.5	1.2	13	110
Tap water (max. allowed) (µg/L)	2.2	0.2	0.2	0.27	3.7

manuscript is one of the few cases dealing with p-NACs, hence adding rare reporting on explosive-contamination.

### Properties of p-NACs and their attenuation

The compounds TNT and DNT are yellowish and odourless, do not exist naturally in the environment and are mainly found associated with the manufacturing of explosives. Both are toxic and the main routes of human exposure are the inhalation of dust particles, ingestion (food) and dermal sorption. Data of studies on human toxicity can be found in the Hazardous Substance Data Base (toxnet.nlm.nih.gov/). The main properties of the targeted p-NACs and the criteria set by the United States Environmental Protection Agency (USEPA) for soil and water are listed in Table 1 (EPA 2012a, b, c, d); the World Health Organization has not yet established drinking water and soil limits for those compounds (WHO 2011). According to EPA (2012a), TNT in residential soils is allowed at concentrations ≤19 mg/kg, above which remediation measures should be undertaken.

The relatively low water solubility, vapor pressure and partition coefficients of TNT (Table 1), imply that fine sediments tend to adsorb it. The TNT that is not adsorbed is usually rapidly degraded under anaerobic conditions (Spain 1995), whereby both biotic and abiotic pathways of degradation occur via reduction of the nitro groups (–NO<sub>2</sub>). DNT has a moderate solubility and a low Henry's coefficient, and tends to remain in water. It is biodegradable under aerobic and anaerobic conditions. As TNT, its relatively low organic-carbon partition coefficient (*K*<sub>oc</sub>) implies a slight

tendency to adsorb onto solids (ATSDR 1998), but preferably to organic materials if the organic carbon fraction constitutes at least 1 % of the soil/sediment on a weight basis (Fetter 1999). Due to their relatively low octanol–water partition (*K*<sub>ow</sub>) coefficients, TNT and DNT are not expected to bio-accumulate significantly, but they can accumulate in plants (ATSDR 1998). Under some conditions, photolysis of TNT and DNT may be significant and fast—the half-life of TNT is up to 22 h (Spangord et al. 1980), and that of the DNT isomers up to 72 h (Mill and Mabey 1985). The toxic compound NT is insoluble and decomposes to toxic gases and oxides of N and of C (Linde 2006).

Attenuation processes are dependent on solubility and dissolution kinetics of the contaminants, transformation and adsorption rates in soils, and biodegradation rates in soils and ground water, mainly. Most processes do not act simultaneously and some only act on certain environmental settings (Brannon and Pennington 2002; Juhasz and Naidu 2007). The permanent structural negative charge of the 2:1 clay minerals gives them the greatest capacity to reversibly bind p-NACs (Haderlein et al. 1996), which is stronger for TNT metabolites than for TNT itself, whereby anaerobic conditions increases the TNT binding capacity (Eriksson 2003). The adsorption capacity of p-NACs by clay minerals increase in the order: kaolinite, illite and montmorillonite (smectite) (Hoehener and Ponsin 2014). In anaerobic soils, TNT transformation is promoted which hinders steady-state conditions. Steady-state conditions are, hence, most likely attained in low organic carbon soils where TNT transformation is less promoted (Pennington et al. 2001).

Parallel to monitoring, several TNT-bioremediation techniques have been promoted worldwide (Boopathy 2000; Lewis et al. 2004; Stenuit et al. 2011), such as bio-venting (Hoehener and Ponsin 2014), or phyto-remediation (Koehler et al. 2002; Rao et al. 2009), that take advantage of TNT and DNT being taken up by plants. Other treatments include soil excavation and treatment by incineration, and in still active explosive production sites draining and treating the lagoon wastewater is a usual procedure (EPA 2014). Kalderis et al. (2011) provides a very good overview over the fate of the explosives in the environment, including a state-of-the-art on remediation techniques.

### **Motivation: fate of the contaminants in the vadose zone and implications for groundwater contamination**

During the course of the previous studies in the area, the vadose zone was not a focus of study. Because contaminants circulate through the vadose zone before reaching the saturated part of the aquifer, it became necessary to examine what was the level and fate of the p-NACs in that part of the aquifer. Hence, the main aim of the present study was to understand the p-NACs distribution in the vadose zone, and to assess its associated potential as a contamination source of groundwater. To understand whether explosives retained in the vadose zone could represent a remnant source of (passive) contamination to groundwater, and how long will it be necessary to naturally and totally remove the contaminants from the unsaturated part of the aquifer, several 1-D simulations of natural attenuation were performed to provide various scenarios of contaminant transport and time required for their total washout. The models used field data and missing data were complemented with literature values.

## **Methods**

### **Sampling**

The sampled (former) wastewater pond was situated inside the production site, upstream and near the previously identified p-NACs “hotspot”, i.e., the most contaminated area (Fig. 1b, Amaral et al. 2009). Two boreholes were drilled down to 9, 30 m apart from each other (Fig. 1c) bored in distinct geo-electric signals (Fig. 2) obtained during a geophysical survey by Time-Domain Electromagnetic methods (for detailed geophysical data and its interpretation see Ramalho et al. 2015). Sediment samples were collected every 1 m, including the very top 35 cm, for the quantification of p-NACs and pH measurement. Every

2 m, samples were taken for the determination of the organic carbon content, the cation exchange capacity (CEC) and particle size. Finally, five samples in total were taken for the screening of other organic compounds. Each sample represents a discrete depth interval, since several centimeters of sediments along the borehole vertical axis were taken for analysis.

### **Laboratorial analysis**

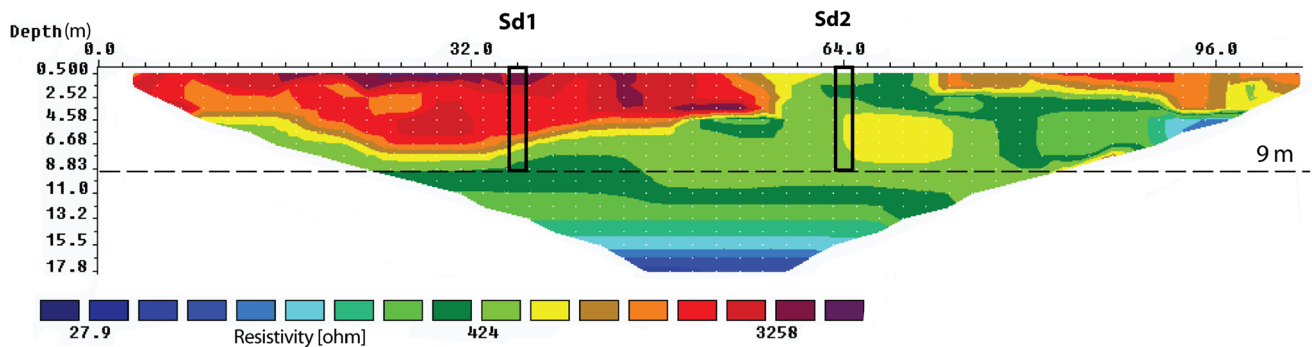
To be able to determine and quantify the p-NACs in the sediments and water, the respective analytical methods were, so far as we know implemented in Portugal for the first time (Gonçalves 2011). In water samples, the extraction of the p-NACs was performed by Solid Phase Extraction—SPE (Alpendurada 2000; Huck and Bonn 2000); SPE is based on the solid-liquid separation that extracts the analytes from the water by adsorption and/or partition for further quantification. The p-NACs were extracted by the Soxhlet extraction technique following EPA’s method SW-846 3540C. This is based on the extraction of the analytes from the sediments by a solvent, transferring them into the liquid phase. The identification and quantification of the individual p-NACs (extracted by the previous methods) were carried out by gas chromatography coupled to mass spectrometry. In the gas chromatograph, the enriched extract is volatilized, and the several analytes are separated in the chromatographic column, entering then into the mass spectrometer for quantification.

The determination of the particle size distribution was obtained by sieving. The cation exchange capacity (CEC) was determined using 1 mol/L ammonium acetate at pH 7, and the total organic carbon (TOC) by wet combustion (Póvoas and Barral 1992). The pH of the sediments was determined in the laboratory after adding distilled water in a ratio 1:2 and after shaking for 5 min. Sediment screening for clays types was performed by diffractometry.

### **One-dimensional modeling**

To find a proper remediation technique and risk-manage contaminated sites it is necessary to understand the fate of the contaminants (Kalderis et al. 2011). To predict the transport of contaminants in the environment, analytical and numerical computer models have been developed, making a fair description of the flow in the unsaturated zone, which is also crucial for prediction of the movement of pollutants into and in the aquifers. Several software packages provided by EPA exist (Mulligan and Yong 2004). In this study, 1-D modeling of the fate of the p-NACs in the sampled vadose zone was performed using *Chemflo-2000* (Nofziger and Wu 2003).





**Fig. 2** Geophysical profile and location of the boreholes drilled in the former wastewater pond (see Fig. 1c). The geophysical profile was obtained by Time-Domain Electromagnetic methods (TDEM) and is a

courtesy of Mohamed Khalil. All obtained geophysical data of the site are discussed in Ramalho et al. (2015)

*Chemflo-2000* uses mathematical models (finite difference methods), where the 1-D water movement (Richards 1931) and chemical transport are given by governing partial differential equations. The 1-D transport in unsaturated media is mainly downwards where the pore water pressures are generally negative caused by surface tension (capillary potential or matric potential), which is a function of the volumetric water content of the soil (Dingman 2002).

*Chemflo-2000* has several limitations: assumes no sources and sinks; the hydraulic conductivity of the soil is unchanged by the presence of a chemical; water loss occurs only at the end of the soil; the partition of the chemical between the solid and liquid phases is proportional, which may not be in real world; and assumes instantaneous and reversible partitioning. Of all limitations, the assumption that the hydraulic conductivity remains unchanged could be the one affecting mostly the model results. It is known, that the presence of the contaminant alters the pore size of the media where it is introduced, and subsequently its hydraulic conductivity (Domenico and Schwarz 1998). Certainly, the disposal of large amounts of compounds into the porous media would have lead, at least in the initial phase of the disposal, to a change in the hydraulic conductivity of the media. Also, adsorption to clays can produce a reduction of the pore size. Probably, water loss occurs also laterally, not only at the end of the soil, when the water table rises in periods of high rainfall rates.

The basic steps for simulating water and chemical movement were: to define the soil/sediment system; to specify the initial and boundary conditions for water and chemicals in the soil; and to define the transport properties (Table 2). It was assumed that water loss from the sediment column occurred by drainage. Modeling aimed at the determination of the time scales for the natural cleanup of the vadose zone, after the sampling date. Thus, the p-NACs concentrations measured in the field were assumed as the

initial concentrations. Simulations for the fate of p-NACs under different boundary conditions were performed. Computer time varied from a few hours to 20 days, being longest for the longest periods modeled.

**Statistics**

Basic statistic analysis was performed and box-plots were used to illustrate the range of the simulated concentration of the contaminants over time and under the conditions set. This permitted a straightforward comparison of the p-NACs distribution in both boreholes.

**Results**

In the studied site, the vadose zone was completely formed by unconsolidated sediments composed of pebbles, sand, silt and clay, whit a few remains of organic matter. Only a few roots at the top 35 cm were observed in that very incipient soil. Sands of various grain sizes (fine sand to gravel) were predominant in both boreholes (Fig. 3). Particles >2 mm size, ranged between 15 and 46 %. In samples <2 mm, sand predominates strongly over clay and silt, by more than 90 %, except the upper most Sd1 sample, that corresponded to a loamy sand. Clay minerals were found in lesser amounts, between roughly 1–10 %, being kaolinite the most identified clay mineral, and, in minor amounts, illite. Smectite was not detected.

The concentration of the total organic carbon, which is food for microorganisms and can act as an adsorbing agent, was measured in the fraction <2 mm. Its content was very low, averaging 0.5 g/kg, i.e. <0.1 % (Table 3). Likewise, the measured CEC was very low in all samples, below the reported standard kaolinite values of 3–15 cmol<sub>c</sub>/kg (Reganold and Harsh 1985). The pH was acidic [Sd1: 4–5; Sd2: 4 with an outlier of 6 at ~8 m depth]. There were no bad smells associated.

**Table 2** Parameters used in the *Chemflo-2000* simulations

Sediments:	Van Genuchten model <sup>a</sup> assumed for water conductivity and water characteristic functions
Texture and length (cm)	Sand, 900
Bulk density (g/cm <sup>3</sup> )	1.55
Organic Carbon (g/g)	0.0005 (mean Sd1 borehole)—Lab. determined
Initial conditions	
Matric potential (cm)	Uniform, −1000 cm, forced to be zero at the bottom of sediment column
Contaminants concentration (see Table 4)	Non-uniform—input of the concentrations obtained from the boreholes, after calculating from µg/kg to g/m <sup>3</sup> (required)
Boundary conditions	
Rainfall (cm/h)	0.00913 (maximum mean rainfall in Lisbon)
	Contaminant free
	Free drainage at the base of the soil column, chemical moves only with the soil solution
Transport properties	
Diffusion coefficient (all compounds) (cm <sup>2</sup> /h)	0.00005 <sup>b</sup>
Dispersion coefficient (default)	2
Partition coefficient (cm <sup>3</sup> /g) ( $K_{oc}$ )	TNT: 12.59, 2,6-DNT: 91, 2-NT: 420
Degradation rate on solid, 1st order (h <sup>-1</sup> )	TNT: 0.000000417/hr (Ehalf-life 190 years) <sup>c</sup>
Mesh size	Every 0.5 cm, 0.05 h, convergence criteria 0.0001
Mass balance errors	0.125 cm and 5 % of maximum relative error

<sup>a</sup> van Genuchten 1980

<sup>b</sup> Valsaraj et al. 1998

<sup>c</sup> Bernstein and Ronen 2012

### The p-NACs in the vadose zone

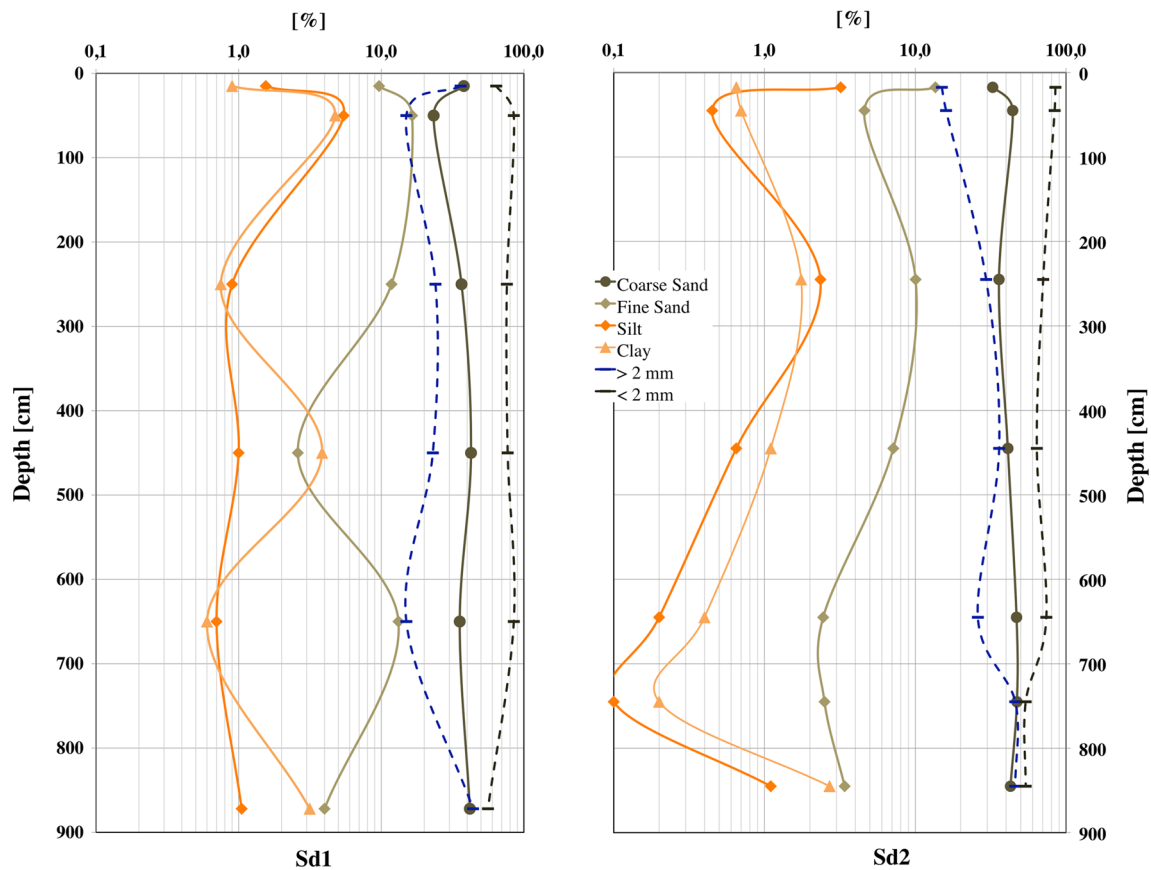
In solid standards recoveries ranged 75–117 % for TNT, DNT-isomers and NT-isomers (Gonçalves 2011). The p-NACs were detected in the sediments at relatively low concentrations and no other organic compound was detected. No trace of TNT crystals was detected at the surface of the ex-pond, which could result from volatilization of the wastewaters. The TNT was the most abundant compound with a median very close to 1000 µg/kg in both boreholes, followed by the total DNTs between 60 and 105 µg/kg or less, and at much lower concentrations by the metabolites NT, which summed up slightly above 10 µg/kg (Figs. 4, 5). Borehole Sd2 showed for each individual p-NACs compound, a broader range of concentration, i.e., stronger variation between maximum and minimum). Roughly, an increase in TNT corresponded to an increase in DNTs and NTs. Only in Sd2 at about 3–4 m depth, did NTs increase significantly (×4) (Fig. 4).

In general, there was no correlation between the grain size type distribution and the bulk relative concentration of the p-NACs. Likewise, no correlation existed between grain size and CEC and the organic carbon content; being an exception the good correlation between the 2,4-DNT and CEC.

### Scenarios of p-NACs fate

The sediment grain size distribution heterogeneity needed to be simplified for modeling purposes. Being sand the main sediment throughout the vadose zone, simulations were performed for a sand column. Table 2 lists the parameters entries in the model and Table 4 lists the p-NACs input concentrations, i.e., those measured in the field, after conversion to unit g/m<sup>3</sup> as required by *Chemflo-2000*. Firstly, the 1-D transport of TNT in borehole Sd1 was simulated for the minimum (600 mm) and maximum (900 mm) mean annual rainfall, to verify differences in the transport velocity of the compound (Fig. 6). The organic-carbon partition coefficient  $K_{oc}$  was set according to Table 2, considering that the p-NACs partitioning is hydrophobic and much of the adsorption of these compounds might occur onto the organic matter contained in the sediments.

In the first 10 years no difference existed between the TNT advection induced by different rainfall values. In fact, a significant difference could only be observed after 50 years. At about 100 years of minimum rainfall, the upper 2 m of the vadose zone would be free of TNT, whereas simulating for the maximum mean annual rainfall, the upper 3 m would be TNT-free after the same time. Since, modeling was mainly run to simulate 100 years, it



**Fig. 3** Vertical distribution of the various sediment grain sizes (<2 mm) obtained along boreholes Sd1 and Sd2. Depicted are also the relative abundances of the bulk sediment particles <2 and >2 mm. Symbols represent the mean depth of the sampled discrete interval

**Table 3** Organic content and cation exchange capacity of the sediments at the discrete depth intervals

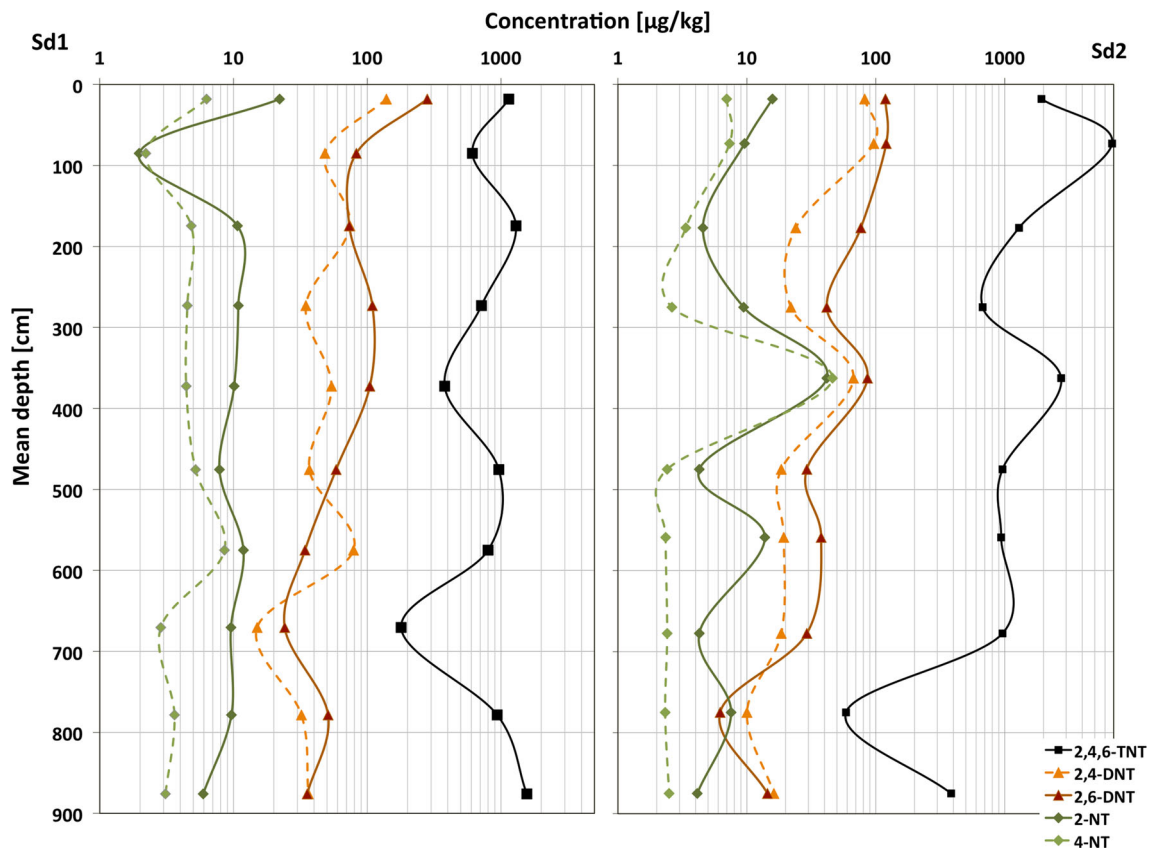
Sample	Depth interval (cm)	Organic content <sup>a</sup> (g/kg)	Cation exchange capacity (cmol <sub>c</sub> kg <sup>-1</sup> )
Sd1	0–30	1.0	0.72
	10–90	0.5	0.38
	200–300	0.2	0.39
	400–500	0.4	1.74
	600–700	0.1	0.43
	844–900	0.2	1.86
Sd2	5–35	0.9	0.91
	0–90	0.7	2.48
	200–290	0.2	0.76
	400–490	0.2	0.93
	600–690	0.1	0.22
	700–790	<0.1	0.04
	800–890	0.2	1.83

<sup>a</sup> Total carbon = organic carbon (Lab. determined)

was decided to use the maximum mean annual rainfall value, thus setting the fastest scenario for the natural cleanup of the site.

Several simulations were then performed for the isolated and simultaneous action of different processes.

Figure 7 depicts the traveling time of TNT in borehole Sd1. Considering advection (rainfall induced) to be the sole process acting on the TNT transport, about 1.5 years would be necessary to fully mobilize TNT out of the vadose zone of the former wastewater pond. [To note that



**Fig. 4** Concentration of the various p-NACs measured at various depths of the vadose zone, in boreholes Sd1 and Sd2. Symbols represent the mean depth of the sampled interval. (Adapted from Gonçalves 2011)

the exact simulation in a silt sediment column would demand 5 years to remove the TNT.] This situation is unrealistic, because by now no more p-NACs would be found in the vadose zone, which is not the case. Assuming that only degradation would act on TNT, there would be virtually no difference on the compound's concentration after 10 years. Thus, degradation rates as reported in the literature (Bernstein and Ronen 2012 and references in Brannon and Pennington 2002) are so slow (even if they vary several orders of magnitude) that their action is negligible on the fate of TNT, hence being insignificant on the mobilization or reduction of that compound. The most representative simulation was the one that combines advection and partition (Fig. 7). Under such conditions, TNT would take at least 100 years to be removed from the upper 3 m (same representation as in Fig. 6 for 900 mm rainfall) and 200 years to be removed from the upper 7 m of the vadose zone. Such a slow removal was also seen in borehole Sd2, as after 100 years the median of TNT concentration was basically the same as by the time of sampling (Fig. 8). In both boreholes, the maximum concentration of TNT steadily decreased overtime. However, in the Sd2 the median remained

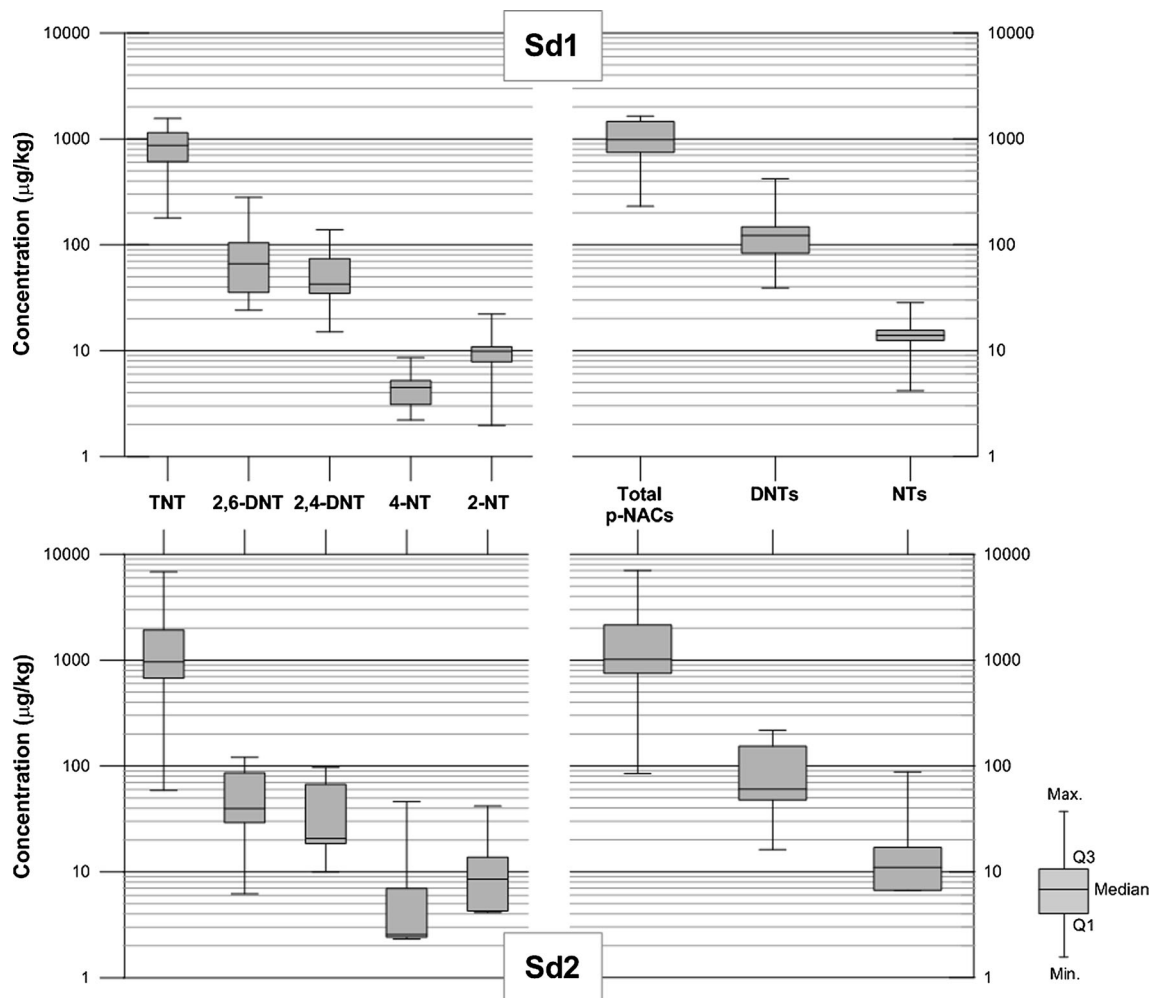
basically unchanged, at around  $1.6 \text{ g/m}^3$ , although the bulk-decrease in the level of contamination (lowering of the maximums and of  $Q_3$  values).

The removal of 2,6-DNT and 2-NT in borehole Sd2 was also modeled combining advection (for maximum mean annual rainfall) and the respective literature's partition coefficients ( $K_{oc}$ ) (Table 2); it was assumed no degradation to occur. Even after 50 and 10 years, the respective very low concentrations of the 2,6-DNT and 2-NT, did not change (Fig. 9). Borehole Sd2 was chosen for most simulations, because of its higher p-NACs content. Likewise, the compounds 2,6-DNT and 2-NT were the selected isomers because of their higher concentrations, thus, in principle, requiring a longer removal time from the vadose zone.

### The water sample

The obtained analytical recoveries in water standards were about 80–100 % for TNT and DNT-isomers and 50–70 % for NT-isomers (Gonçalves 2011). One of the collected samples, the deepest of borehole Sd2, was water-saturated. It was unclear whether that water was part of the local





**Fig. 5** Statistical box-plot of the concentration of the individual p-NACs, total p-NACs, and sum of the isomers of DNT and NT, at boreholes Sd1 and Sd2

water table, if it was part of a small water lenses, or if it was capillary water, since there were no measurements of the water table around the pond, due to the lack of piezometers. The geophysical profiles showed significant lower resistivity below 14 m depth, which could be the general water table (Ramalho et al. 2015), thus, probably the water sample was part of the capillary fringe. Nevertheless, that pore-water was sampled and analyzed for p-NACs. The concentrations obtained were plotted against those in the sediments of the same sample, assuming chemical equilibrium existed between both phases (Fig. 10)—the concentration in the sediments is higher than in the water. Because there was only a single data point of concentration in the solid and in the aqueous phase, no distribution coefficient  $K_d$  of the p-NACs could be calculated, which would have permitted to determine a retardation rate of the compounds within the solid matrix of the vadose zone.

### Discussion

Two boreholes provide insufficient data and do not fully represent a broad contaminated area. The collected data, however, does give an insight into what is expected to be found in the vadose zone of the most contaminated spots within the SPEL site, i.e., the former wastewater disposal ponds. Because, no absolute values on waste amounts disposed over time are available on that particular sampled wastewater pond, no mass balance can be performed. The mass balances obtained refer solely to the model data, considering the input data (field) and the output data (model).

The sediments sampled at depth in the former wastewater pond, revealed a very incipient soil, without horizons. This is more or less expected in quartz sands where minimal chemical weathering occurs (Krauskopf and Brid 1995). The soil bare of vegetation could have been affected

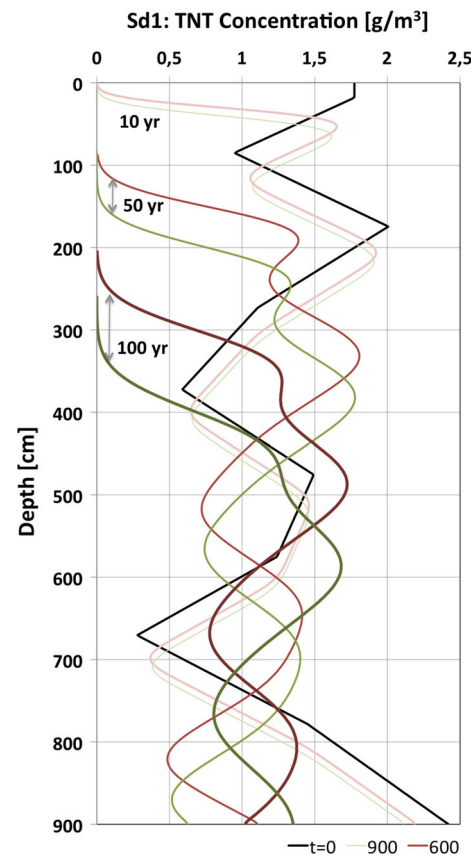
**Table 4** Input concentrations of TNT, 2,6-DNT and 2-NT in boreholes Sd1 and Sd2, at the mean sampled depths, after calculation to  $\text{g/m}^3$  (using the bulk density of soil of  $1550 \text{ kg/m}^3$ ), as required for Chemflo-2000

Sd1			
Mean depth (cm)	2,4,6-TNT ( $\text{g/m}^3$ )		
18	1.773		
85	0.947		
174.5	2.007		
273	1.108		
372.5	0.588		
475.5	1.493		
575	1.241		
670.5	0.278		
778.5	1.452		
876	2.420		
Sd2			
Mean depth (cm)	2,4,6-TNT ( $\text{g/m}^3$ )	2,6-DNT ( $\text{g/m}^3$ )	2-NT ( $\text{g/m}^3$ )
18	2.990	0.184	0.024
73	10.557	0.187	0.015
177	2.003	0.119	0.007
275	1.046	0.065	0.015
362.5	4.251	0.134	0.065
475	1.490	0.045	0.007
559	1.456	0.058	0.021
677.5	1.490	0.045	0.007
775	0.091	0.010	0.012
875	0.596	0.022	0.006

by the toxicity of the TNT (and DNT) that may have prevented vegetation to grow (Travis et al. 2008).

The predominance of sands (of various grain sizes) over clays (and silt), the very low organic matter content (hence, weak native fertility), lead to a weak ability to retain moisture and nutrients, which resulted in very low CEC. Low organic-carbon content hinders transformation and consequently a steady state to be reached. Moreover, only kaolinite and illite were detected. Smectite, which is the clay type that most efficiently holds p-NACs, was not detected and sorption is not expected to greatly retard the transport of the p-NACs. The natural attenuation potential of the sediments apparently is low. The concentration of the p-NACs and other measured parameter did not correlate with the distribution of grain sizes.

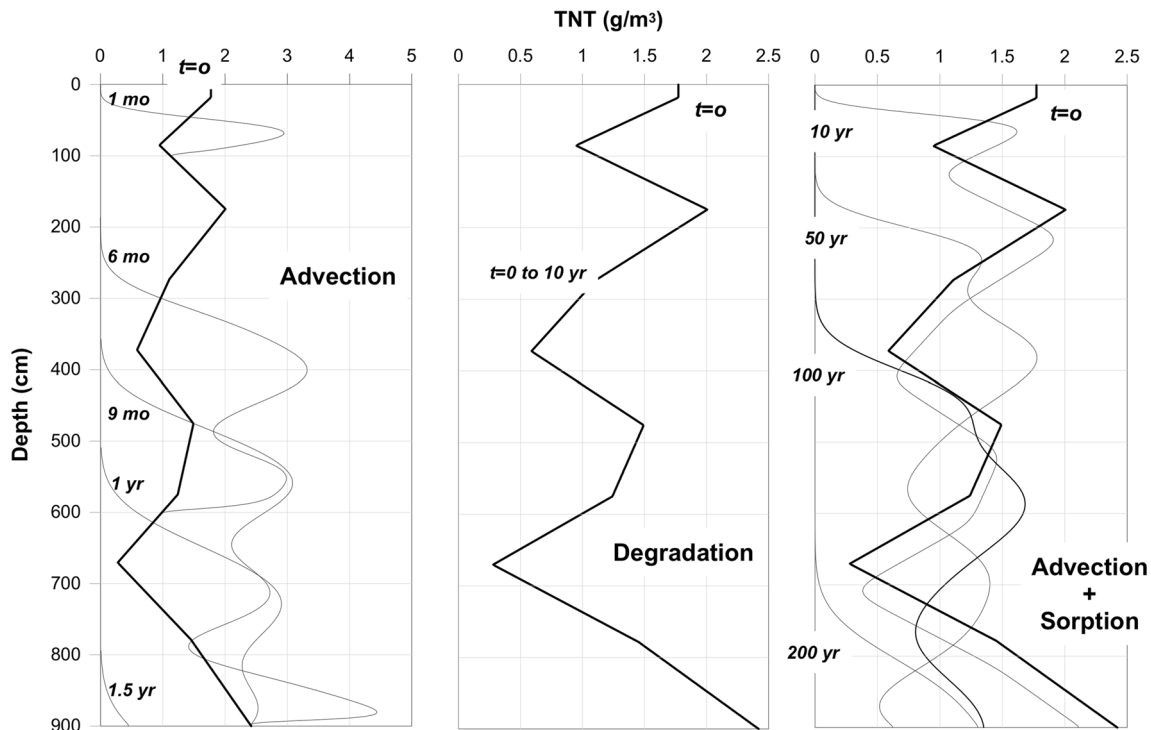
The small % of finer sediments attributes the sediment column permeability to air and water. Such permeability to gas fluxes, could have allowed oxygen to enter the pores of



**Fig. 6** Simulation of TNT transport (combined advection and partition) in the vadose zone (borehole Sd1) for the minimum (600 mm, *dashed line*) and maximum (900 mm, *solid line*) mean annual precipitation values for Lisbon. The *thick black line* represents the TNT concentration measured in the sediments. Note that the concentration of TNT is now given in  $\text{g/m}^3$ , the unit required for Chemflo-2000

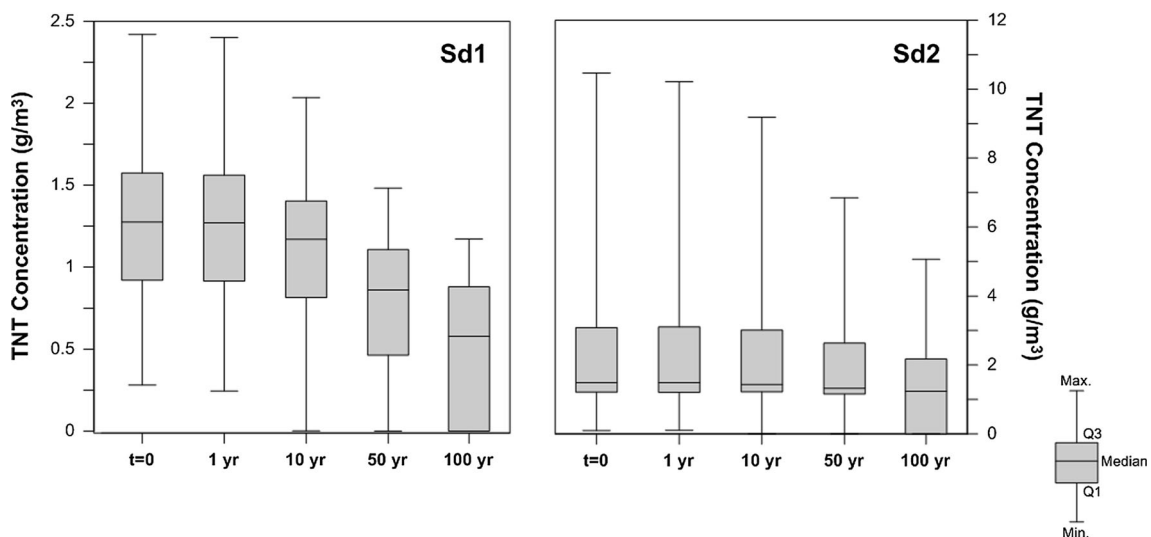
the vadose zone, once the pond dried (due to site inactivity), thus hindering the degradation of TNT and DNT. Moreover, oxygen in the vadose zone decreases the TNT binding capacity (Eriksson 2003). However, the presence of NT can only be justified as a result of the mass transformation of TNT and/or DNT, since it was not manufactured at the site. The presence of metabolites assures that contamination was attenuated over time due to mass transformation; however, this process was not efficient to totally remove TNT and DNT, as TNT remains in the vadose zone as the main contaminant. The very low concentrations of NT, followed by those of DNT, could also be explained by the higher water solubility of those compounds in comparison to TNT (Table 1), thus being more easily washed-out from the vadose zone.

The median of the concentrations of TNT, DNT-isomers and NT isomer were similar for both boreholes and their absolute concentrations did not vary much at depth. The variations observed reacted accordingly, i.e., they



**Fig. 7** Simulation of TNT movement in the vadose zone sampled in borehole Sd1, using *Chemflo-2000*. Shown are the times of TNT removal for scenarios of advection only, degradation only and

advection and sorption acting simultaneously. The concentration of TNT is given in  $\text{g/m}^3$  as required for *Chemflo-2000*



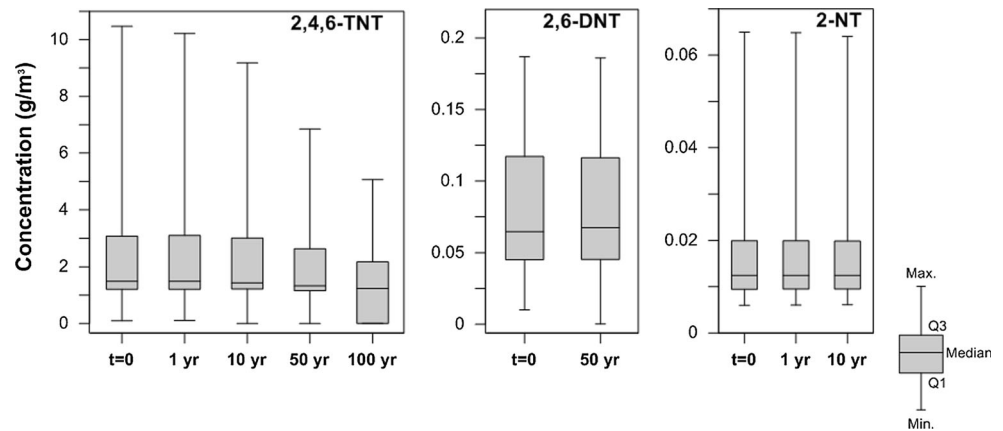
**Fig. 8** Box-plots of the simulated removal time of TNT from the vadose zone within the former wastewater pond, using the concentrations determined in boreholes Sd1 and Sd2. The concentration of TNT is given in  $\text{g/m}^3$  as required for *Chemflo-2000*

diminished and augmented at the same depths—a peak in TNT concentrations would be accompanied by an increase in the other compounds, if a change would be observed. In fact, in borehole Sd2, TNT increased greatly at 3–4 m depth, and so did the other p-NACs, mainly NT, suggesting that at that depth there were at some point more favorable

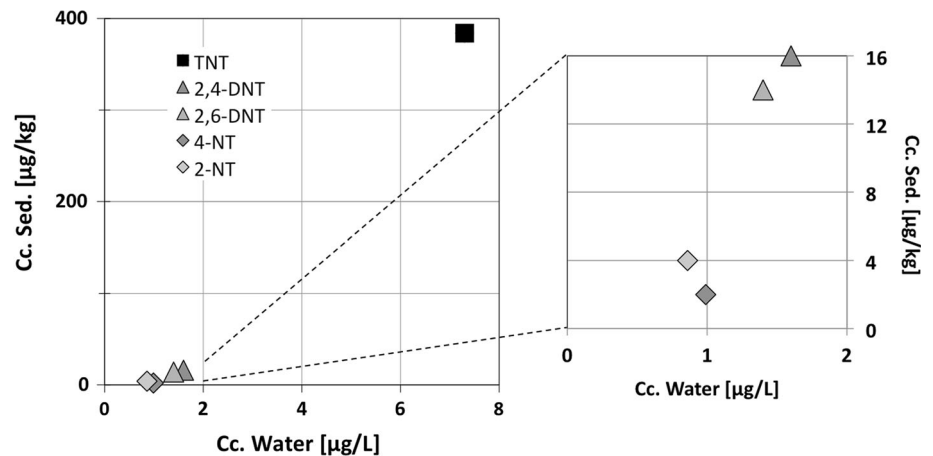
conditions for degradation to take place. At 7–8 m depth, the TNT concentration decreased greatly being solely accompanied by 2,6-DNT, suggesting both compounds underwent the same attenuation process.

Despite the heterogeneous grain sizes, the p-NACs distribution is basically homogeneous with some

**Fig. 9** Box-plots of the simulated removal time of the p-NACs TNT, 2,6-DNT and 2-NT, using the concentrations determined in borehole Sd2. The model parameters are listed in Table 2. The p-NACs' concentrations are given in  $\text{g}/\text{m}^3$  as required by Chemflo-2000



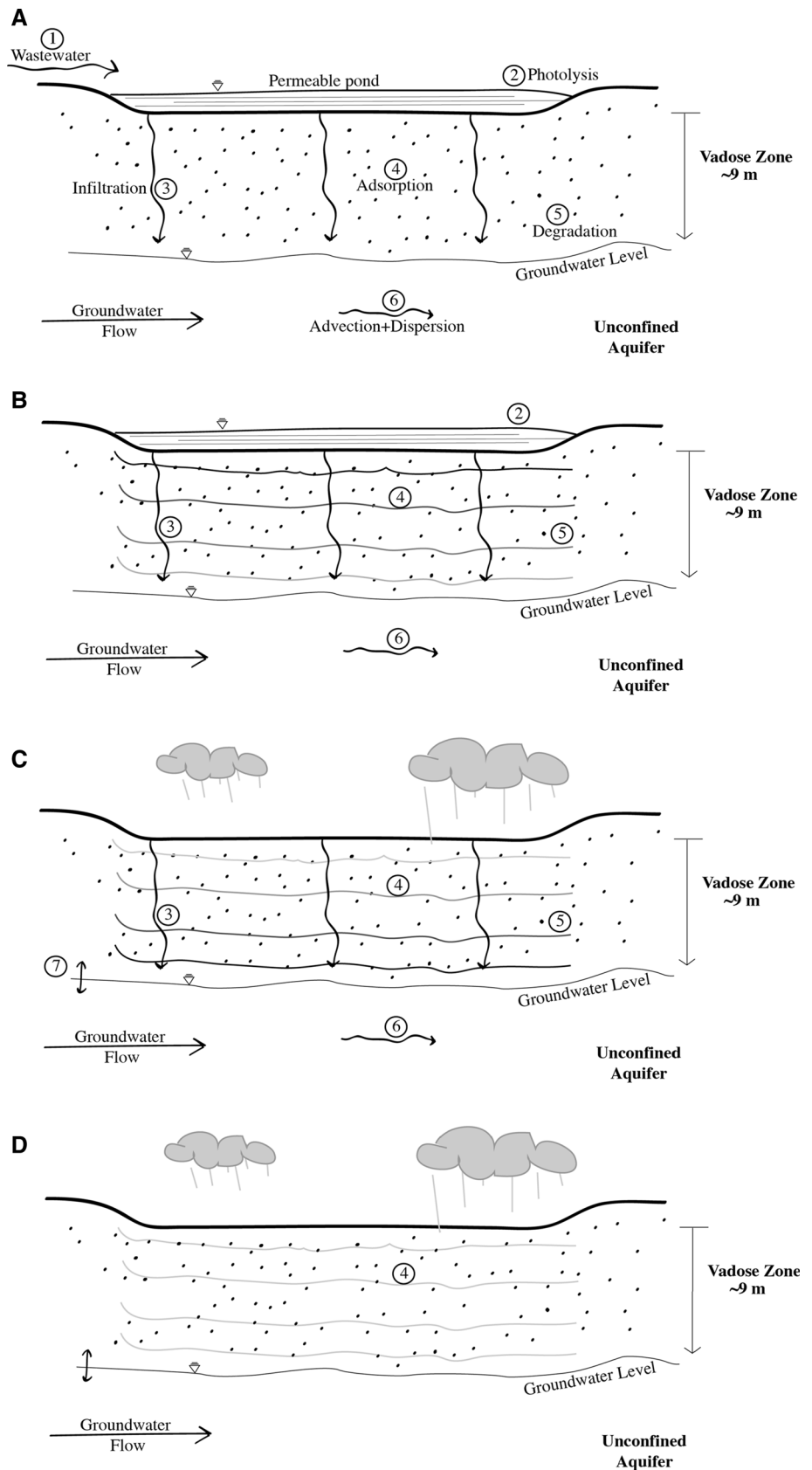
**Fig. 10** Concentrations of the p-NACs in the sediments and the porous aqueous phase of a sample taken in Sd2 at about 8.7 m depth. The right panel is a zoom of the left one for NT and DNT isomers



concentration lows and highs at discrete depths. This is supposed to be the result of the thorough washout of the sediments over time, down to the lowest concentration possible. In fact, the concentrations of the p-NACs measured are below the limits set by EPA for remediation demands. The limiting values for residential soils (see Table 1) are higher than the measured concentrations (TNT max.: 6.8  $\text{mg}/\text{kg}$ ; 2,4-DNT max.: 0.14  $\text{mg}/\text{kg}$ ; 2,6-DNT max.: 0.28  $\text{mg}/\text{kg}$ ; 2-NT max.: 0.042  $\text{mg}/\text{kg}$ , and 4-NT max.: 0.046  $\text{mg}/\text{kg}$ ). Only 2,6-DNT was measured at concentrations near to EPA's limits (EPA 2012a), at the top-most part of the Sd1 borehole. Thus, in principle, and according to the only official limits found in the literature, the contaminated land within the studied area seems not to require remediation, as the pollutants are detected at relatively low concentrations. Such low level of p-NACs contamination (considering the large amount of p-NACs disposal), suggests that natural attenuation by dispersion due to wastewater infiltration, has removed the largest amount of p-NACs from the vadose zone. Attenuation occurred during >50 years of wastewater disposal, followed by 15 years of site inactivity and total closure.

To summarize, Fig. 11 schematically illustrates a conceptual model on the fate of the p-NACs on the vadose zone of the former wastewater pond. Stage A represents the situation during the production of explosives at the site: the disposal of the wastewater (1) to the excavated permeable pond. The p-NACs in the artificial pond would either undergo photolysis (2) or would infiltrate (3) to the groundwater. In the vadose zone, the p-NACs could undergo partition to the solid matrix or be degraded (4). The part that reached the saturated part of the unconfined aquifer was transported by advection and/or dispersion. Stage B—cease of the wastewater discharge, but the pond would be filled with water that infiltrated into the ground, leading to a progressive change in the concentration of the contaminants (as represented by the color gradient, where the darker the color the higher the concentration). In Stage C, the pond dried and only rain mobilized the p-NACs remaining in the vadose zone, down to the aquifer. Under such conditions most attenuation processes could still occur and the p-NACs concentration was less at the upper levels of the sediment column as they moved downwards. Stage D represents the ongoing situation. The p-NACs

**Fig. 11** Conceptual model of the fate of the p-NACs in the studied vadose zone of the former wastewater pond. See text for description of the various stages





have been washed-out from the vadose zone and the remaining concentration is very low (light color). Probably the remaining concentration is due to the partition of the p-NACs onto the solid particles and to the organic material. Such strong sorption will take several decades of rainfall to be broken, and allow the whole p-NACs to be removed naturally.

The 1-D simulations suggested, the p-NACs were only removed down to a certain threshold concentration, after which no natural process seems to efficiently (in this case, rapidly) act on the complete removal of the compounds from the vadose zone. Surely such low remnant concentration no longer, if ever did, interferes on the hydraulic conductivity of the vadose zone, hence not limiting the *Chemflo-2000* result. It is, thus, suggested that the vadose zone contains today the least concentration possible to attain under the action of natural processes, representing the part of the contamination that could not be removed naturally. Simulations of advection under the action of rainfall combined with reported partition coefficients, showed reduction of TNT concentration further down, virtually removing it totally from the vadose zone only after 200 years.

Thus, any soil treatment should be engineered according to the site-specific conditions (Kalderis et al. 2011), for example by promoting the growth of indigenous plants and of bacteria (Rylott et al. 2011). As the wastewaters were exposed at the surface, photolysis of the explosives could have been relevant in TNT mass reduction; however, no such evidence was found.

The total p-NAC concentration in the pore water collected in this study (12.15 µg/L) is much lower than that of the well-water (~31 mg/L) collected during the study by Amaral et al. (2009). Sample 560, was a 'hotspot' sample, one of the most contaminated representing the upper aquifer just downstream of the SPEL area and the nearest well to the former wastewater pond where the pore-water was collected. If any comparison is possible, one can simplistically affirm that most p-NACs contamination lies now in the groundwater, after having been washed-out from the sediments.

## Conclusions

Fifteen years after the end of the production of explosives at the studied site, the p-NACs were found in very low concentrations in the vadose zone of a former wastewater pond. The main contaminant TNT was detected at roughly 10 times higher concentrations than DNT and about 100 times higher than NT. The presence of this metabolite clearly indicates that natural transformation has taken place, but it was not efficient to totally remove the main contaminant TNT. The quite homogeneous distribution of

the p-NACs throughout the vadose zone of the former pond indicated a thorough 'washout' of the compounds by rainfall-induced transport from the unsaturated part to the saturated part of the (contaminated) upper aquifer of the area. Such washout down to levels below legal limits, and the very long time for total removal of the p-NACs, leads to the hypothesis that the concentrations measured, correspond to values under which, and no longer, natural processes act efficiently reducing contamination at the site. As simulated by 1-D modeling with *Chemflo-2000*, TNT could take 200 years to be totally removed, while DNT and NT would not decrease at all after a considerable amount of human time-scale.

By modeling, another insight into the fate of the p-NACs in the studied site was obtained, complementing the groundwater contamination studies performed previously (Amaral et al. 2009). From both studies (vadose zone and groundwater), it can be concluded that the major contamination problem lies in the groundwater rather than in the vadose zone. Further surveys should be conducted in other contaminated areas of the former explosive production site, to ascertain that conclusion.

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